

Translational invariance of Coulomb series and symmetric potentials in crystals

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(Dated:)

It is shown that Coulomb series are to be considered within a special mode of summation so as to describe bulk properties of crystals. The translational invariance is then an explicit integral property of Coulomb series that is tantamount to the effect of invariant periodic boundary conditions discussed earlier. Absolute bulk potentials with zero mean value are then substantiated as a unique solution in the general case of triclinic lattices. An invariant treatment of the bulk Coulomb energy follows therefrom. The potential symmetry is verified for simple point-charge lattices and is connected with the centre of gravity of the potential field that is relevant to non-local charges as well.

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I. INTRODUCTION

Sums of Coulomb potentials over lattices [1] are basic for describing the cohesive energy of solid state [2, 3, 4, 5, 6, 7, 8]. Such sums also determine local potentials responsible for the electronegativity and charge transfer in crystals [6, 9, 10, 11, 12, 13, 14, 15, 16] and so specify the electronic band structure [7, 8, 9, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27].

The problem which still exists is to determine bulk Coulomb series so that the result of summation in all the above events be unique in every particular case. The potential symmetry is then evident at least in the simplest point-charge lattices of AB type [9, 28, 29, 30, 31, 32]. Therefore, the bulk Coulomb energy can be specified by particular values of the absolute local potentials therein [3, 28, 30, 33, 34, 35, 36, 37, 38, 39, 40]. However, different modes of summation with various types of parametrization either in the direct space [28, 31, 34, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50] or with making use of the reciprocal one [3, 33, 38, 45, 51, 52, 53, 54, 55, 56] lead to controversial results. This fact is due to the conditional character of convergence of infinite Coulomb series [1, 57, 58].

To be unique, the bulk solution of interest must, certainly, be independent of the optional parameters of the mode of summation [28, 43, 44, 45, 59]. As a hint about it, surface effects are to be irrelevant to bulk properties [8, 20, 28, 31, 33, 44, 46, 49, 59, 60, 61, 62]. All the statistical treatment of solids is based on this statement [63, 64, 65]. Zero mean bulk potential is declared therefrom regardless of the summation scheme [8, 20, 33, 36, 38, 43, 56, 59, 61, 66, 67]. But it is neither the case of parent infinite series [68, 69] nor the case of periodic boundary conditions [63, 70] while they may be modified by a constant potential as an available periodic solution of Laplace's equation [18, 26, 43, 59].

As found [71, 72], the solution of interest arises under periodic boundary conditions invariant to the definition

of the unit cell relative to the crystal structure, which generalize the translational invariance based on periodic replications of a certain basic unit cell [8, 20, 59, 73, 74, 75]. This result substantiates Ewald's proposal [33] to exclude the uniform potential component [59, 60, 74] as well as the energy effect of surface polarization [73, 74, 76, 77] from the results of summation that was not convincing for a long time [8, 19, 20, 43, 74, 78, 79, 80, 81, 82].

Moreover, though the energy value for a neutral unit cell in the bulk is formally independent of any conceivable change in the potential origin [8, 61, 62, 74, 83, 84], the bulk Coulomb energy and absolute bulk potentials appear to be functionally connected. The fact that electrostatic quantities in the bulk are independent of real surfaces implies that the configuration of any surface is to be consistent with the bulk state [5, 9, 22, 49, 61, 76, 85, 86, 87, 88, 89]. In particular it means that the surface conditions have to reproduce the bulk state in question [41, 61, 69, 90].

It is important that the same problem is relevant to the definition of direct bulk Coulomb series as such. Indeed, pristine Coulomb series, albeit expressed in terms of periodic charge distributions, do not contain the periodicity as a property of summation in an explicit fashion [33]. In the present paper we deduce that invariant periodic boundary conditions actually imply a special mode of summation as a continuous procedure with piecewise smooth intermediate boundary surface and with the further averaging of the oscillating result over the period specified by lattice translations. As shown, apart from the convergence conditions, an additional one should be imposed on the charge distribution per unit cell so as to represent Coulomb series in a conventional form. As an example, the symmetric potentials in cubic crystals are readily calculated in an effective manner. The topological nature of the potential symmetry is discussed.

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II. AMBIGUITY ABOUT ABSOLUTELY CONVERGENT COULOMB SERIES

If $\rho(\mathbf{r})$ is a certain charge distribution attributed to a unit cell, then the direct Coulomb sum associated with $\rho(\mathbf{r})$ and describing the electrostatic potential at the point \mathbf{r} can be written as

$$U_{\text{Cd}}(\mathbf{r}) = \sum_i' \int_V \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_i|}, \quad (1)$$

where i runs over the Bravais lattice composed of the unit-cell origins \mathbf{R}_i , the integral is over the volume V occupied by $\rho(\mathbf{r}')$, which can spread beyond the unit-cell volume [6, 21, 23, 26, 27, 29, 47], the prime on the summation sign implies missing the contribution of any point charge if it happens at \mathbf{r} . For the absolute convergence of (1), $\rho(\mathbf{r})$ is supposed to obey the following constraints [20, 31, 34, 43, 48, 51, 59, 60, 67, 74, 91]:

$$\int_V \rho(\mathbf{r}) d\mathbf{r} = 0, \quad (2)$$

$$M_\mu \equiv \int_V r_\mu \rho(\mathbf{r}) d\mathbf{r} = 0, \quad (3)$$

$$G_{\mu\nu} \equiv \int_V r_\mu r_\nu \rho(\mathbf{r}) d\mathbf{r} = 0 \quad \text{at} \quad \mu \neq \nu, \quad (4)$$

$$G_{xx} = G_{yy} = G_{zz} = H, \quad (5)$$

where r_μ are Cartesian co-ordinates of \mathbf{r} , H is a certain constant. Condition (2) ensuring the local neutrality is conventional. Relations (3)–(5) can be maintained by symmetry [8, 17, 34, 43, 59, 60, 66]. If they do not hold for any initial $\rho^{\text{ini}}(\mathbf{r})$ [8, 22, 24, 34, 60, 79, 84, 91, 92], $\rho^{\text{ini}}(\mathbf{r})$ can always be modified properly [71, 72]. The implication is that the electrical neutrality is the only fundamental constraint in crystals [8, 20, 33, 35, 51, 55, 68, 76, 80, 81, 93], but a rather arbitrary charge distribution $\rho^{\text{ini}}(\mathbf{r})$ transformed into $\rho(\mathbf{r})$ driven by (2)–(5) with an optional H may be adopted for the purpose of the lattice summation specified as a definite procedure in (1) [21, 28, 33, 46, 51].

The residual effect of H is evident from the mean potential value \bar{U}_{Cd} associated with (1) and it is independent of the order of summation due to (2)–(5). Following Bethe [94], we have

$$\bar{U}_{\text{Cd}} = -\frac{2\pi}{3v} \int r^2 \rho(\mathbf{r}) d\mathbf{r} = -\frac{2\pi H}{v}, \quad (6)$$

where v is the volume of the unit cell, the left equality of (6) is typical [8, 17, 20, 69, 74, 82, 84, 95] and is further converted with the help of (5). We see that the value of \bar{U}_{Cd} turns out to be optional through H . This inference can be naturally extended to the potential $U_{\text{Cd}}(\mathbf{r})$ as such [20, 69]. However, it is also clear that the effect of H is artificial and should be removed.

Although the case of $H = 0$ is of great importance, as will be clear later on, it does not exhaust the situation

at hand. To gain insight into this problem, we turn to the limiting behaviour of (1) upon the direct summation over closed shells of one unit cell thickness, enveloping a reference unit cell in a consecutive fashion. According to (2)–(5), such an order of summation is not more demanded by the arguments of convergence [20, 26, 28, 33, 34, 35, 39, 46, 49, 51, 52, 55, 58, 60, 73, 76, 96], but allows for the equal uniformity along each crystallographic axis [21, 51, 59, 61, 69]. The absolute convergence of (1) implies that the contribution of remote shells with numbers $m \geq m_c \gg 1$ is negligible:

$$\lim_{m_c \rightarrow \infty} \sum_{m=m_c}^{\infty} \sum_{i_m} \int_V \frac{\rho(\mathbf{r}) d\mathbf{r}}{|\mathbf{R}_{i_m} + \mathbf{r}|} = 0, \quad (7)$$

where i_m runs over the unit cells belonging to the m th shell. Relation (7) persists as long as remote unit cells are added as permanent bricks described by $\rho(\mathbf{r})$ [8, 20, 22, 34, 44, 59, 60, 61, 68, 69, 82, 86, 91]. Since individual features of such bricks have to be lost in the crystal interior [20, 34, 44, 59], the fortuitous contribution of H to the lattice sum is patently generated by outer shells of summation [20, 59, 82] and so must be eliminated as irrelevant to bulk properties now.

III. CONTINUITY OF SUMMATION AND INVARIANT PERIODICITY

Inasmuch as (7) holds due to the discrete character of summation over shells there, it is reasonable to modify this type of summation so as to remove that discreteness, but without destruction of the charges taken into account [20, 40, 66, 93]. To this end, we conceive that our crystal is enclosed in an imaginary large bounding box homothetic to the unit cell, with a reference unit cell at its centre, and the summation region is restricted by the box volume. The summation over shells is then treated as a continuous procedure of enlarging this box. In a triclinic lattice with the lattice parameters a , b and c along unit vectors \mathbf{e}_a , \mathbf{e}_b and \mathbf{e}_c , the evolution of the bounding box can be described by the parameters A , B and C corresponding to \mathbf{e}_a , \mathbf{e}_b and \mathbf{e}_c and increasing linearly in an evolution parameter f at

$$\frac{A}{a} = \frac{B}{b} = \frac{C}{c} \gg 1, \quad (8)$$

as shown schematically in Fig. 1(a).

The event of $\rho(\mathbf{r})$ arranged within the unit-cell parallelepiped is first considered. The limiting procedure in (7) can then be readily associated with the bounding-box evolution if we imagine that the m_c th shell is truncated by the bounding box at a given moment. It implies that the inner part of this shell gives an additive contribution to the maternal sum over $m < m_c$ and this shell is removed from (7) and replaced by the next one when its outer boundary is achieved by the bounding box. The periodicity of the latter events upon the evolution in

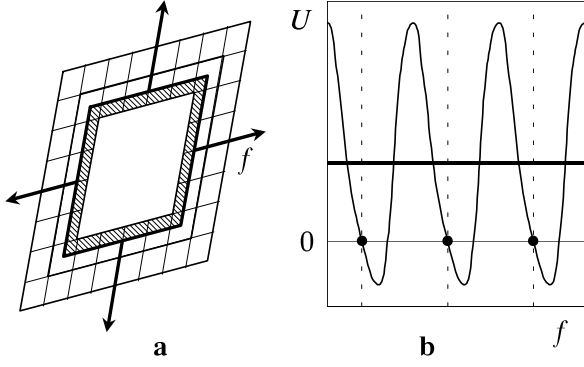


FIG. 1: Summation over the shells as a uniform continuous procedure: (a) Remote unit cells, small regular parallelograms, are united into the shells bordered by heavier lines, with the hatched area of an incomplete outermost shell truncated by the bounding box depicted by the heaviest lines. The bounding-box interior contributing to the lattice sum enlarges uniformly upon increasing the evolution parameter f . (b) Oscillations of the limiting value of a certain inner potential U as a function of f are expected relative to its magnitude specified by complete outermost shells. This initial magnitude marked by the filled circles is treated as an origin, for convenience. Averaging over oscillation periods shown by vertical dotted lines converts the oscillating U into an invariant value depicted by the heavy horizontal line, of which position describes the potential shift of interest.

question reflects the translational invariance of (7) accompanied by some periodic change in the value of the resulting maternal sum, as sketched in Fig. 1(b). This limiting effect can naturally be analysed within a single period of oscillations at $0 \leq f \leq 1$, so that f becomes a measure of the incorporated share of the m_c th shell.

Note that now the expected result depends on our summation mode exhibiting the translational invariance as an integral property of Coulomb series [33]. To make the above oscillations surely finite and minimal, all the faces and edges of the bounding box are assumed to be so charged as to retrieve local constraints (2) and (3) for the truncated unit cells at every moment of the bounding-box evolution. Then the potential effect of the remote charged edges of the truncated m_c th shell modified by charges on the corresponding edges of the bounding box vanishes because it is specified by the mean charge densities [28, 59, 60, 61, 85], which are zero by definition.

To discuss the contribution of the modified m_c th shell faces to (7), we focus on the \mathbf{A} th face disposed in the \mathbf{e}_a direction, with \mathbf{R}_i describing the unit cells on this face. Here we are interested in the potential contribution at the centre of the bounding box. In the expansion of the integrand in (7) in powers of r/R_i , the ratio of moduli, only terms linear in the components $R_i^\perp \mathbf{A}$ of \mathbf{R}_i along an outward normal to the \mathbf{A} th face survive [46, 61, 85, 86]. Their contribution to (7) can be written as

$$\Phi_{\mathbf{A}}(f) = \frac{\Omega^2}{\sin \beta} \int_{-a/2}^{t(f)} dt \int_{-b/2}^{b/2} dp \int_{-c/2}^{c/2} du \rho(t, p, u)$$

$$\times [t(f) - t] \sum_{i \in \{\mathbf{A}\}} \frac{R_i^\perp \mathbf{A}}{R_i^3}, \quad (9)$$

where $t(f) = af - a/2$, $\mathbf{r} = t\mathbf{e}_a + p\mathbf{e}_b + u\mathbf{e}_c$,

$$\Omega = [1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma]^{1/2} \quad (10)$$

at $(\mathbf{e}_a \mathbf{e}_b) = \cos \alpha$, $(\mathbf{e}_b \mathbf{e}_c) = \cos \beta$ and $(\mathbf{e}_c \mathbf{e}_a) = \cos \gamma$.

The averaging of $\Phi_{\mathbf{A}}(f)$ over the period of oscillations is readily defined in the form

$$\bar{\Phi}_{\mathbf{A}} = \int_0^1 \Phi_{\mathbf{A}}(f) df \quad (11)$$

and is the final logical step of elimination of the summation boundary, because the boundary which has neither definite structure nor definite position does not more exist. This case is naturally associated with the topologically endless lattice. Indeed, the same result is valid for the contribution $\bar{\Phi}_{-\mathbf{A}}$ of the $-\mathbf{A}$ th face of the m_c th shell by symmetry, but their combination may be represented as

$$\int_0^1 [\Phi_{\mathbf{A}}(f) + \Phi_{-\mathbf{A}}(1-f)] df = 2\bar{\Phi}_{\mathbf{A}}, \quad (12)$$

where the integrand corresponds to the closure of the lattice in the \mathbf{e}_a direction along the $\pm \mathbf{A}$ th bounding-box faces, in which case these auxiliary bounding-box faces merge and so neutralize each other by definition, but periodic boundary conditions arise instead. The averaging over f in (12) then implies the invariance of the periodic boundary conditions to the optional position of the plane of joining inside particular unit cells [71, 72].

On determining $\bar{\Phi}_{\mathbf{B}}$ and $\bar{\Phi}_{\mathbf{C}}$ in the same manner and taking our previous result [71, 72] into account, for the total potential eliminating the boundary effect we obtain

$$\Phi_{\text{top}} = 2(\bar{\Phi}_{\mathbf{A}} + \bar{\Phi}_{\mathbf{B}} + \bar{\Phi}_{\mathbf{C}}) = \frac{2\pi H}{v}. \quad (13)$$

Note that issue (13) is relevant to the foregoing periodic boundary conditions, which hold for each basic crystallographic direction and so are three-dimensional. The duality of the treatment of the procedure of averaging makes this inference geometrically noncontradictory.

It is significant that like (6), result (13) is independent of the particular features of the crystal symmetry. Owing to the obvious additivity of the potential effect, result (13) can be extended to overlapping $\rho(\mathbf{r})$, as well as to more complicated Bravais lattices of higher symmetry. By induction, the validity of (13) can also be extended to events of $\rho(\mathbf{r})$ spreading to infinity as long as the basic statements that H is finite and that the stationary limiting regime is provided by (7) are maintained. As a result, the general concept that a rather arbitrary $\rho^{\text{ini}}(\mathbf{r})$ can be involved for describing a crystal [20, 30, 80, 98] is substantiated.

TABLE I: Tentative unit-cell point charges s_j in units of κ for each of n_L primitive cubic lattices, with the charge positions generated from those indicated, in units of a , in the parentheses by virtue of cubic transformations.

Crystal	n_L	$s_1(0,0,0)$	$s_2(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$s_3(\frac{1}{2}, 0, 0)$	$s_4(\frac{1}{2}, \frac{1}{2}, 0)$	$s_5(-\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$	$s_6(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$s_7(1, 0, 0)$	$s_8(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$	$s_9(\frac{3}{2}, \frac{3}{2}, \frac{3}{2})$
CsCl	1	$\frac{337}{256}$	—	—	—	—	$-\frac{513}{4096}$	$-\frac{27}{512}$	—	$\frac{1}{4096}$
NaCl	4	$\frac{32}{23}$	—	$-\frac{7}{46}$	$-\frac{3}{92}$	—	$-\frac{1}{92}$	—	—	—
ZnS	4	$\frac{415}{384}$	$-\frac{3}{16}^a$	—	$-\frac{1}{144}$	$-\frac{1}{48}^a$	—	$\frac{1}{2304}$	—	—
Cu ₂ O	4 ^b	$\frac{17}{8}$	$-\frac{3}{8}^c$	—	$-\frac{3}{32}$	$-\frac{3}{64}^c$	—	—	$\frac{1}{64}^c$	—
CaF ₂	4	$\frac{35}{16}$	$-\frac{49}{256}$	—	$-\frac{1}{64}$	$-\frac{5}{256}$	—	—	—	—
BiF ₃	4	$\frac{591}{184}$	$-\frac{1}{4}$	$-\frac{61}{368}$	$-\frac{13}{736}$	—	$-\frac{1}{1472}$	—	—	—

^aThese charges are at the proper tetrahedral positions only.

^bThe final structure is made up of primitive lattices rotated about a fourfold symmetry axis.

^cThese charges are on $(1, 1, 1)$ diagonals only.

TABLE II: As a result of the direct summation over point-charge cubic lattices, the absolute bulk potentials U_{bj} , in units of κ/a , at the unit-cell symmetric points specified in the parentheses and the Madelung constant α_M (the bulk energy \mathcal{E}_b described by (16) in units of $-\kappa^2/a$). The positive ion is at the $(0, 0, 0)$ point. The repeating potential values are indicated in symbols.

Crystal	$U_{b1}(0,0,0)$	$U_{b2}(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$U_{b3}(-\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$U_{b4}(\frac{1}{2}, 0, 0)$	$U_{b5}(\frac{1}{2}, \frac{1}{2}, 0)$	$U_{b6}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	α_M
CsCl	-2.03536151	0 ^a	U_{b2}^a	0.48658923 ^a	-0.48658923 ^a	2.03536151	2.03536151
NaCl	-3.49512919	0 ^a	U_{b2}^a	3.49512919	U_{b1}	U_{b4}	3.49512919
ZnS	-3.78292610	3.78292610	0.28779691 ^a	-0.28779691 ^a	U_{b1}	U_{b4}^a	3.78292610
Cu ₂ O	-3.78292610	6.47653093	0.55497170 ^a	-0.28779691 ^a	U_{b1}	U_{b4}^a	10.25945703
CaF ₂	-7.56585221	4.07072302	U_{b2}	-0.57559383 ^a	U_{b1}	U_{b4}^a	11.63657523
BiF ₃	-11.06098140	4.07072302	U_{b2}	2.91953536	U_{b1}	U_{b4}	22.12196279

^aThe corresponding lattice positions are interstitial.

Note that our procedure of averaging the potential effect of the bounding-box evolution resembles antecedent approaches [28, 31, 34, 36, 43, 44, 86], which might be associated with the averaging over a symmetric set of discrete points on the oscillatory potential curve.

According to (1) and (13), the bulk potential field in a crystal is as follows:

$$U_b(\mathbf{r}) = U_{Cd}(\mathbf{r}) + \Phi_{top}. \quad (14)$$

Although relationship (14) is anticipated [38, 59], the topological treatment of Φ_{top} [71, 72] differs from earlier interpretations [19, 97]. On combining (14) and (6), for the mean bulk potential we obtain the expected result $\bar{U}_b = 0$. Hence, $U_b(\mathbf{r})$ defined by (14) is independent of H and does not contain any uniform component. The potential symmetry follows therefrom.

IV. DISCUSSION

We may apply (13) and (14) to the rapidly convergent direct Coulomb summation [48] for several cubic point-charge structures with the lattice spacing a and with charges measured in units of κ , the modulus of a minimal point charge. These structures are treated as

decomposed into n_L primitive lattices [5, 99] with the unit-cell charges compiled in Table I. According to (13), for each structure in question we obtain

$$\Phi_{top} = \frac{\pi\kappa}{a} \times \begin{cases} 4(s_6 + s_7 + 9s_9) & \text{CsCl} , \\ 4(s_3 + 4s_4 + 4s_6) & \text{NaCl} , \\ 2(s_2 + 8s_4 + 11s_5 + 8s_7) & \text{ZnS} , \\ (s_2 + 16s_4 + 11s_5 + 9s_8) & \text{Cu}_2\text{O} , \\ 4(s_2 + 4s_4 + 11s_5) & \text{CaF}_2 , \\ 4(s_2 + s_3 + 4s_4 + 4s_6) & \text{BiF}_3 \end{cases} \quad (15)$$

as the summary topological contribution of all n_L sublattices. The resulting numerical values calculated through (1) for each local potential specified by (14) at some symmetric points are arranged in Table II, where (15) retrieves the potential symmetry [1, 5, 30, 100].

Of course, dealing with an arbitrary $\rho^{\text{ini}}(\mathbf{r})$, it is reasonable to go over to $\rho(\mathbf{r})$ specified by $H = 0$. Then the boundary effects are formally excluded and the analysis is available in terms of direct sums only. In this case $U_b(\mathbf{r}) = U_{Cd}(\mathbf{r})$ that explains Evjen's approach [34] to NaCl, for example. Moreover, the bulk Coulomb energy \mathcal{E}_b per unit cell can then be confidently written in terms of (1) in a conventional manner

[8, 21, 33, 40, 51, 52, 73, 78]:

$$\begin{aligned}\mathcal{E}_b &= \frac{1}{2} \int_V d\mathbf{r} \rho(\mathbf{r}) \sum_i' \int_V \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_i|} \\ &= \frac{1}{2} \int_V d\mathbf{r} \rho(\mathbf{r}) U_b(\mathbf{r}) = \frac{1}{2} \int_{V^{\text{ini}}} d\mathbf{r} \rho^{\text{ini}}(\mathbf{r}) U_b(\mathbf{r}),\end{aligned}\quad (16)$$

in agreement with (14). The last relation in (16) is due to the absolute character of the potential field $U_b(\mathbf{r})$ and, in general, implies that every charge distribution consistent with the crystal structure may be incorporated there, if we are interested in the value of \mathcal{E}_b at given $U_b(\mathbf{r})$. In particular, the Madelung constants in Table II are obtained with making use of the potentials $U_{bj}(\mathbf{r})$ on integer point charges, in agreement with the corresponding precise data [1, 4, 30, 46, 93, 96, 101, 102, 103, 104]. Bearing in mind [71, 72] that the customary functional relation [8, 14, 52]

$$\frac{\delta \mathcal{E}_b}{\delta \rho^{\text{ini}}(\mathbf{r})} = U_b(\mathbf{r}) \quad (17)$$

holds for (16) as a base for the self-consistent determination of $\rho^{\text{ini}}(\mathbf{r})$ [4, 8, 14, 21, 22, 24], any difficulties [15, 20, 62, 73, 80, 93] in defining \mathcal{E}_b are obviated via (16).

The topological effect of Φ_{top} is evident in the hypothetical case of lattices composed of non-interacting neutral atoms, which are to be spherical and non-overlapping for this purpose [105]. In the simplest event [40, 52, 78, 98, 106, 107], we consider such atoms as solid spheres of radii r_0 , charged uniformly, with neutralizing positive nuclear charges Z at their centres. One atom per unit cell is assumed. Then relations (2)–(5) hold by symmetry. According to (5) and (13), we derive

$$\Phi_{\text{top}} = -\frac{2\pi Z r_0^2}{5v}. \quad (18)$$

On the other hand, the sum in (1) is reduced to a sole term if \mathbf{r} is inside an atom and is zero otherwise [105]. The calculation of the mean value \bar{U}_{Cd} is then straightforward and we get

$$\bar{U}_{\text{Cd}} = \left(\frac{4\pi r_0^3}{3v} \right) \bar{U} \quad \text{at} \quad \bar{U} = \frac{3Z}{10r_0}, \quad (19)$$

where \bar{U} is the mean intratomic potential, the factor in the parentheses renormalizes \bar{U} per v . According to (14), (18) and (19), we reach $\bar{U}_b = 0$ again. However, as a centre of gravity [8, 13, 19, 67], Φ_{top} now connects intratomic potentials which dwell as formally independent in the case at hand. It is worth noting that

this effect of (18) is absent in low-dimensional lattices [20, 37, 46, 83, 91] where $\Phi_{\text{top}} = 0$. But such a negative shift due to delocalization of electrons in atoms and ions is a general effect which, apart from the effects of ionic overlap [20, 21, 29], modifies the three-dimensional point-charge lattice potentials. According to estimate (18), this shift is compared to potentials in Table II and may account for trapping small atoms and ions at interstices [38, 108, 109, 110, 111] as well as for the asymmetry of vacancy concentrations [10, 112, 113, 114, 115, 116].

Note that every artificial delocalization of charges [25, 29, 33, 40, 52, 54, 56, 61, 86, 97, 98] always produces a certain potential shift of the discussed nature, with including uniform charge distributions [8, 33, 68, 69, 78, 82, 83, 91]. For instance, according to (5) and (13), in the case of simple cubic lattices a uniform charge background with the total charge Q per unit cell gives rise to $\Phi_{\text{top}} = \pi Q/6a$. This term compensates the ordinary background effect [82]. However, such contributions cancel out in the superposition if, for example, two identical sublattices composed of unlike charges, but with common parameters of charge delocalization are studied [33].

V. CONCLUSION

In summary, a special mode of summation associated with invariant periodic boundary conditions must be included in the definition of Coulomb lattice series so as to describe bulk properties of crystals. As a result, absolute electrostatic potentials arise as a unique solution of interest. Zero mean bulk potential ensuring this uniqueness within every summation scheme devised to date is substantiated rigorously. Based on absolute bulk potentials, the invariant treatment of the bulk Coulomb energy is proposed. The limiting cases estimated highlight the potential symmetry as a peculiar feature of the three-dimensional potential map.

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[1] M.L. Glasser, I.J. Zucker, in *Theoretical Chemistry: Advances and Perspectives*, edited by H. Eyring, D. Hen-

derson (Academic Press, New York, 1980), Vol. 5, p. 67.
[2] J. Sherman, Chem. Rev. **11**, 93 (1932).

- [3] B.R.A. Nijboer, F.W. De Wette, *Physica* **23**, 309 (1957).
- [4] T.C. Waddington, in *Advances in Inorganic Chemistry and Radiochemistry*, edited by H.J. Emeléus, A.G. Sharpe (Academic Press, New York, 1959), Vol. 1, p. 157.
- [5] M.P. Tosi, in *Solid State Physics*, edited by F. Seitz, D. Turnbull (Academic Press, New York, 1964), Vol. 16, p. 1.
- [6] M.G. Trefry, E.N. Maslen, M.A. Spackman, *J. Phys. C* **20**, 19 (1987).
- [7] J. Ihm, *Rep. Prog. Phys.* **51**, 105 (1988).
- [8] P. Bagno, L.F. Donà dalle Rose, F. Toigo, *Adv. Phys.* **40**, 685 (1991).
- [9] J.D. Levine, P. Mark, *Phys. Rev.* **144**, 751 (1966).
- [10] W. Van Gool, A.G. Piken, *J. Mater. Sci.* **4**, 105 (1969).
- [11] J.C. Wang, *J. Chem. Phys.* **73**, 5786 (1980).
- [12] M. Satoh, T. Taki, *Phys. Rev. B* **23**, 6732 (1981).
- [13] M.A. Spackman, R.F. Stewart, in *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, edited by P. Politzer, D.G. Truhlar (Plenum Press, New York, 1981), p. 407.
- [14] K.A. Van Genechten, W.J. Mortier, P. Geerlings, *J. Chem. Phys.* **86**, 5063 (1987).
- [15] R.J. Cole, P. Weightman, *J. Phys.: Condens. Matter* **9**, 5609 (1997).
- [16] A.F. Kohan, G. Ceder, *Phys. Rev. B* **57**, 3838 (1998).
- [17] J. Callaway, M.L. Glasser, *Phys. Rev.* **112**, 73 (1958).
- [18] W.E. Rudge, *Phys. Rev.* **181**, 1020 (1969).
- [19] R.N. Euwema, G.T. Surratt, *J. Phys. Chem. Solids* **36**, 67 (1975).
- [20] F.E. Harris, in *Theoretical Chemistry: Advances and Perspectives*, edited by H. Eyring, D. Henderson (Academic Press, New York, 1975), Vol. 1, p. 147.
- [21] R. Dovesi, C. Pisani, C. Roetti, V.R. Saunders, *Phys. Rev. B* **28**, 5781 (1983).
- [22] J.G. Ángyán, B. Silvi, *J. Chem. Phys.* **86**, 6957 (1987).
- [23] G.H. Schadler, *Phys. Rev. B* **45**, 11314 (1992).
- [24] R.D. King-Smith, D. Vanderbilt, *Phys. Rev. B* **47**, 1651 (1993).
- [25] K. Fuchizaki, *J. Phys. Soc. Japan* **63**, 4051 (1994).
- [26] X.-G. Zhang, W.H. Butler, J.M. MacLaren, J. Van Ek, *Phys. Rev. B* **49**, 13383 (1994).
- [27] M. Alatalo, M. Weinert, R.E. Watson, *Phys. Rev. B* **60**, 7680 (1999).
- [28] S.K. Roy, *Can. J. Phys.* **32**, 509 (1954).
- [29] J. Birman, *Phys. Rev.* **97**, 897 (1955).
- [30] W. Van Gool, A.G. Piken, *J. Mater. Sci.* **4**, 95 (1969).
- [31] J.V. Calara, J.D. Miller, *J. Chem. Phys.* **65**, 843 (1976).
- [32] H. Xiaoguang, H. Meichun, L. Hong, *J. Phys.: Condens. Matter* **4**, 5977 (1992).
- [33] P.P. Ewald, *Ann. Phys. F4* **64**, 253 (1921).
- [34] H.M. Evjen, *Phys. Rev.* **39**, 675 (1932).
- [35] K. Højendahl, *Kgl. Danske Videnskab. Selskab, Math.-Fys. Medd.* **16**(2), 133 (1938).
- [36] I.D.C. Gurney, *Phys. Rev.* **90**, 317 (1953).
- [37] O. Emersleben, *Z. Phys. Chem.* **204**, 43 (1955).
- [38] F.E. Harris, H.J. Monkhorst, *Phys. Rev. B* **2**, 4400 (1970).
- [39] K.F. Taylor, *J. Comput. Chem.* **8**, 291 (1987).
- [40] D.N. Argyriou, C.J. Howard, *Aust. J. Phys.* **45**, 239 (1992).
- [41] E. Madelung, *Phys. Z.* **19**, 524 (1918).
- [42] F.C. Frank, *Philos. Mag.* **41**, 1287 (1950).
- [43] J.P. Dahl, *J. Phys. Chem. Solids* **26**, 33 (1965).
- [44] F.Y. Hajj, *J. Chem. Phys.* **70**, 4369 (1979).
- [45] V. Massidda, *Physica B* **114**, 327 (1982).
- [46] H. Coker, *J. Phys. Chem.* **87**, 2512 (1983).
- [47] A. Gonis, E.C. Sowa, P.A. Sterne, *Phys. Rev. Lett.* **66**, 2207 (1991).
- [48] I.G. Fisenko, E.V. Kholopov, *Phys. Stat. Sol. (b)* **173**, 515 (1992).
- [49] D. Wolf, *Phys. Rev. Lett.* **68**, 3315 (1992).
- [50] L. Vitos, J. Kollár, *Phys. Rev. B* **51**, 4074 (1995).
- [51] O. Emersleben, *Phys. Z.* **24**, 73 (1923).
- [52] F. Bertaut, *J. Phys. Radium* **13**, 499 (1952).
- [53] C.A. Sholl, *Proc. Phys. Soc.* **92**, 434 (1967).
- [54] A. Sugiyama, *J. Phys. Soc. Japan* **53**, 1624 (1984).
- [55] R.E. Crandall, J.P. Buhler, *J. Phys. A* **20**, 5497 (1987).
- [56] B.A. Luty, I.G. Tironi, W.F. Van Gunsteren, *J. Chem. Phys.* **103**, 3014 (1995).
- [57] P. Epstein, *Math. Ann.* **56**, 615 (1903).
- [58] D. Borwein, J.M. Borwein, K.F. Taylor, *J. Math. Phys.* **26**, 2999 (1985).
- [59] A. Redlack, J. Grindlay, *J. Phys. Chem. Solids* **36**, 73 (1975).
- [60] C.K. Coogan, *Aust. J. Chem.* **20**, 2551 (1967).
- [61] D.M. Heyes, F. Van Swol, *J. Chem. Phys.* **75**, 5051 (1981).
- [62] R.M. Martin, G. Ortiz, *Phys. Rev. B* **56**, 1124 (1997).
- [63] M. Born, K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).
- [64] J.M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960).
- [65] R.B. Griffiths, *Phys. Rev.* **176**, 655 (1968).
- [66] A.K. Jain, M.P. Verma, *Phys. Stat. Sol. (b)* **102**, 705 (1980).
- [67] P. Herzig, *Theor. Chim. Acta* **67**, 323 (1985).
- [68] D.M. Heyes, *J. Chem. Phys.* **74**, 1924 (1981).
- [69] L. Kleinman, *Phys. Rev. B* **24**, 7412 (1981).
- [70] M. Born, Th. von Kármán, *Phys. Z.* **13**, 297 (1912).
- [71] E.V. Kholopov, Preprint 2001-01 (Inst. of Inorg. Chem., Novosibirsk, 2001).
- [72] E.V. Kholopov, cond-mat/0203530.
- [73] S.W. De Leeuw, J.W. Perram, E.R. Smith, *Proc. R. Soc. London A* **373**, 27 (1980).
- [74] G. Makov, M.C. Payne, *Phys. Rev. B* **51**, 4014 (1995).
- [75] P.A. Schultz, *Phys. Rev. B* **60**, 1551 (1999).
- [76] E.R. Smith, *Proc. R. Soc. London A* **375**, 475 (1981).
- [77] K. Yokogawa, Y. Nomura, G. Iwata, *J. Phys. C* **18**, 2033 (1985).
- [78] F.W. De Wette, *Phys. Rev. B* **21**, 3751 (1980).
- [79] R. Frech, *Phys. Rev. B* **32**, 6832 (1985).
- [80] J. Olives, *Phys. Stat. Sol. (b)* **138**, 457 (1986).
- [81] M.W. Deem, J.M. Newsam, S.K. Sinha, *J. Phys. Chem.* **94**, 8356 (1990).
- [82] M. O'Keeffe, J.C.H. Spence, *Acta Crystallogr. A* **50**, 33 (1994).
- [83] J. Ihm, M.L. Cohen, *Phys. Rev. B* **21**, 3754 (1980).
- [84] R. Restori, *Chem. Phys.* **143**, 57 (1990).
- [85] P.W. Tasker, *J. Phys. C* **12**, 4977 (1979).
- [86] W.W. Lee, S.-I. Choi, *J. Chem. Phys.* **72**, 6164 (1980).
- [87] R.E. Watson, M.L. Perlman, J.W. Davenport, T.K. Sham, *Solid State Commun.* **41**, 151 (1982).
- [88] K. Kokko, P.T. Salo, R. Laihia, K. Mansikka, *Phys. Rev. B* **52**, 1536 (1995).
- [89] M. Plihal, D.C. Langreth, *Phys. Rev. B* **58**, 2191 (1998).
- [90] J.K. Mackenzie, *J. Chem. Phys.* **26**, 1769 (1957).
- [91] G.L. Hall, *Phys. Rev. B* **19**, 3921 (1979).

- [92] M. Satoh, T. Taki, Phys. Rev. B **23**, 6711 (1981).
- [93] R.E. Crandall, J.F. Delord, J. Phys. A **20**, 2279 (1987).
- [94] H. Bethe, Ann. Phys. F4 **87**, 55 (1928).
- [95] P. Becker, P. Coppens, Acta Crystallogr. A **46**, 254 (1990).
- [96] S. Bhowmick, D. Roy, R. Bhattacharya, Chem. Phys. Lett. **148**, 317 (1988).
- [97] Z. Su, P. Coppens, Acta Crystallogr. A **51**, 27 (1995).
- [98] P. Herzig, Chem. Phys. Lett. **68**, 207 (1979).
- [99] F. Hund, Z. Phys. **94**, 11 (1935).
- [100] C.H. Leung, K.S. Song, Physica B **114**, 323 (1982).
- [101] G.C. Benson, F. Van Zeggeren, J. Chem. Phys. **26**, 1083 (1957).
- [102] Y. Sakamoto, J. Chem. Phys. **28**, 164 (1958).
- [103] Q.C. Johnson, D.H. Templeton, J. Chem. Phys. **34**, 2004 (1961).
- [104] B. Sarkar, K. Bhattacharyya, Chem. Phys. Lett. **150**, 419 (1988).
- [105] J.D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, New York, 1962).
- [106] E.F. Bertaut, J. Phys. Chem. Solids **39**, 97 (1978).
- [107] G.L. Hall, Phys. Rev. B **24**, 2881 (1981).
- [108] J.R. Macdonald, A.P. Lehnen, D.R. Franceschetti, J. Phys. Chem. Solids **43**, 39 (1982).
- [109] J. Isoya, H. Kanda, Y. Uchida, Phys. Rev. B **42**, 9843 (1990).
- [110] J.E. Lowther, Phys. Rev. B **51**, 91 (1995).
- [111] A.A. Bonapasta, Phys. Rev. B **58**, 10378 (1998).
- [112] P. Bogusławski, E.L. Briggs, J. Bernholc, Phys. Rev. B **51**, 17255 (1995).
- [113] W.A. Oates, G. Eriksson, H. Wenzl, J. Alloys Comp. **220**, 48 (1995).
- [114] P. Piquini, R. Mota, T.M. Schmidt, A. Fazzio, Phys. Rev. B **56**, 3556 (1997).
- [115] I. Gorczyca, A. Svane, N.E. Christensen, Phys. Rev. B **60**, 8147 (1999).
- [116] E.V. Kholopov, Zh. Struct. Chim. **43**, 600 (2002).